Oxidizable conversion-based assessment of per- and polyfluoroalkyl substances (PFASs) in wastes and their related products

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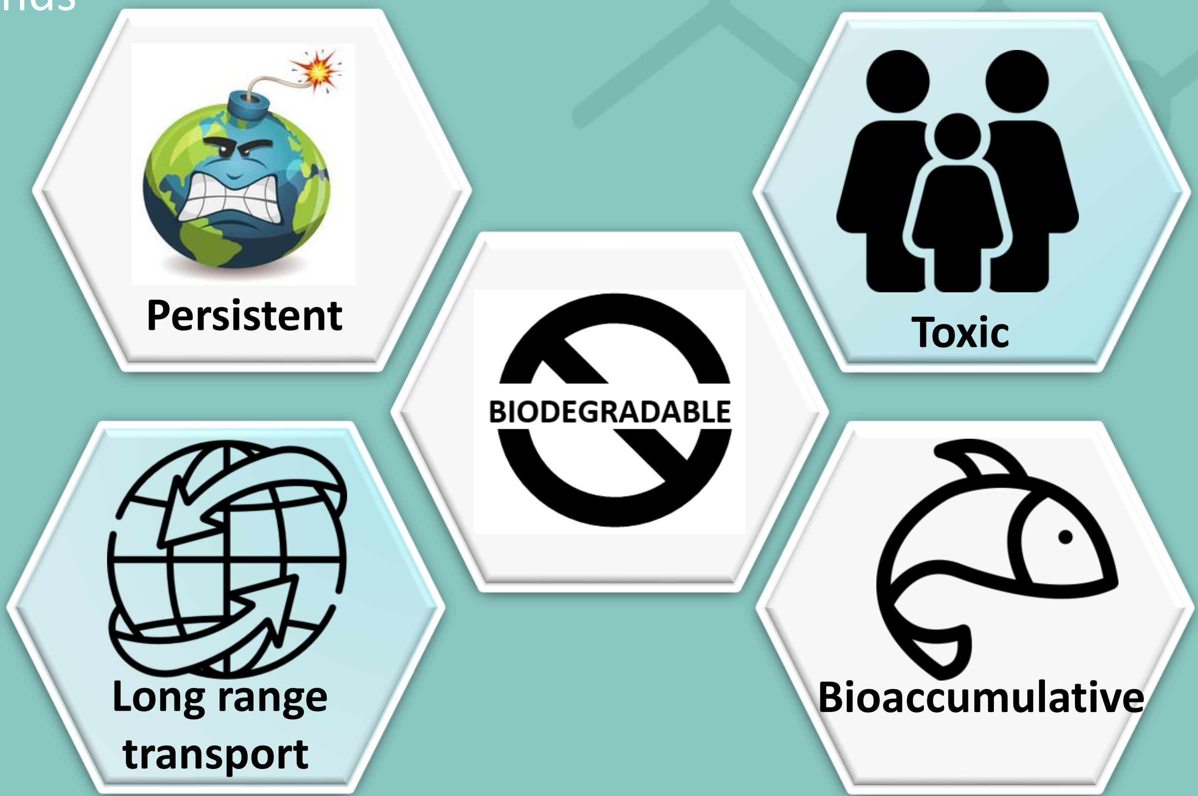
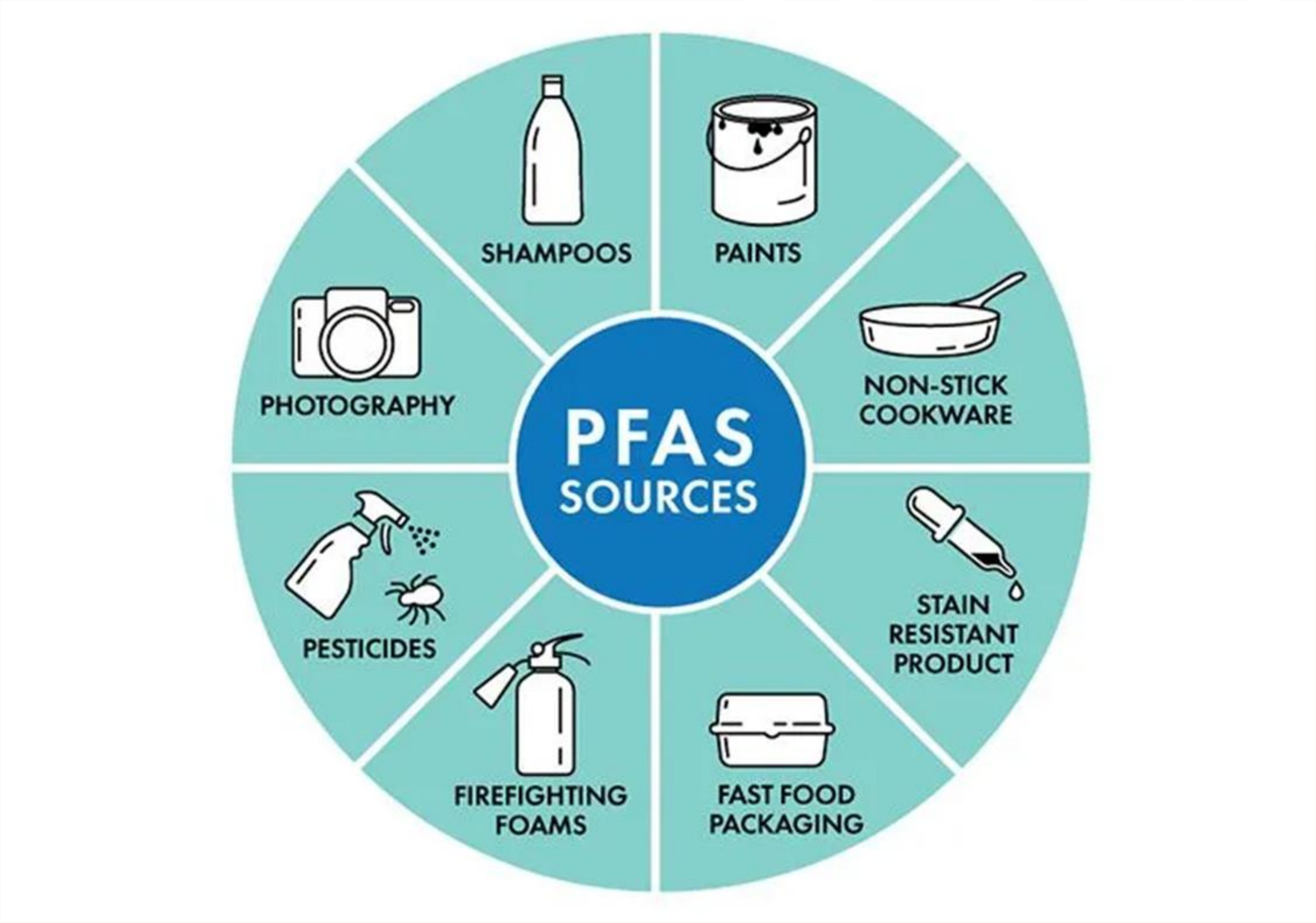
What are PFASs?

- Per-and polyfluoroalkyl substances (PFASs)
- Synthetic organic compounds
- Hydrocarbon backbone where multiple or all of the hydrogen atoms in the structure are replaced with fluorine
- Strong C-F bonds

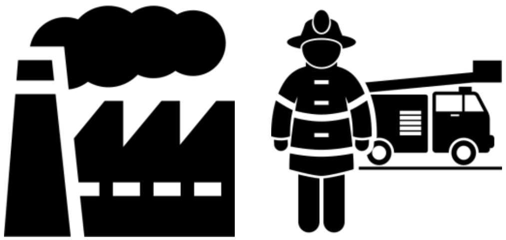


PFAS sources



https://www.hartcoenvironmental.com/teledyne-isco-wastewater-samplers-are-being-used-for-pfas-monitoring

How are we exposed to PFASs?



Occupational exposure

Consumer products containing PFASs

Inhaling PFAS-contaminated dust

Consequences of exposure to PFASs[1]

- Decreased birth weight
- Increased risk of cancer
- Hormone disruption and increased risk for thyroid disease
- Changes in liver enzymes

Fetuses are exposed through the umbilical cord

Ingesting PFAS-contaminated food and drinking water

Infants are exposed to PFAS through breast milk

[1] https://www.atsdr.cdc.gov/pfas/health-effects/index.html

Problem statement

- There is limited information about the actual PFASs including perfluoroalkyl acids (PFAAs) precursors and their potential oxidative conversion products present in most product samples such as firefighting foams and materials coated with DWR products.

- For example[1]:
  "proprietary hydrocarbon surfactant"
  "proprietary fluorosurfactant"

- Moreover, it is estimated that 90% of the PFAS pool in the environment are potential perfluoroalkyl acids (PFAAs) precursors[2].

- As a result:
  a. the likelihood of underestimating the total amount of PFASs discharged into the environment is high
  b. controlling PFASs emissions and lowering the risks to human health and the environment becomes difficult

[1] https://www.chemguard.com/pdf/fire-suppression/datasheets/C303.pdf

[2] https://one.oecd.org/document/ENV/JM/MONO(2018)7/en/pdf

Problem statement

- Furthermore, time-consuming and expensive analytical techniques are used to identify PFAS and/or PFAA precursors present in samples.

For example;

Suspect and non-target analysis using HRMS

↓ Identified unknowns

Target analysis using known reference standards

- Therefore, there is a need for a cost-effective approach for the determination of PFAS including PFAA precursors not only in product samples but also in environmental samples.

[1] https://one.oecd.org/document/ENV/JM/MONO(2018)7/en/pdf

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Objectives

- To optimize the original Total Oxidizable Precursor (TOP) assay method (Houtz&Sedlak, 2012)[1] and the USEPA 3rd Draft Method 1633[2]
- To investigate the presence of PFASs including PFAA precursors in Durable Water repellents and firefighting foams using the optimized methods
- To investigate the generation behavior of PFAAs during TOP assay

[1]Houtz&Sedlak (2012)
https://doi.org/10.1021/es302274g
[2]https://www.epa.gov/system/files/documents/2021-09/method_1633_draft_aug-2021.pdf

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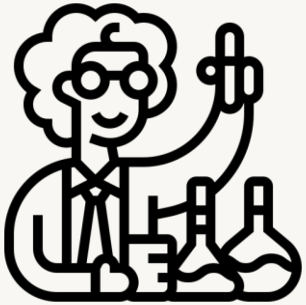

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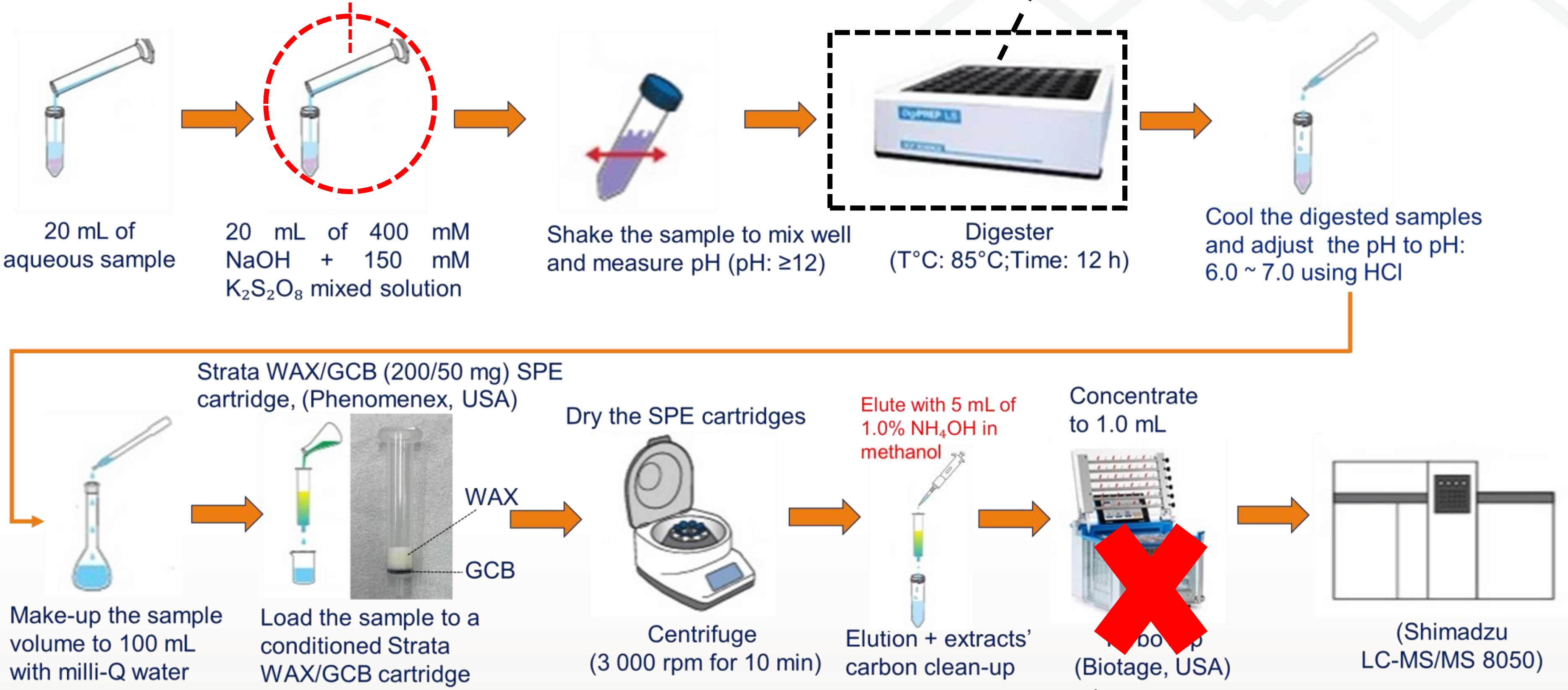
Optimized TOP assay and USEPA method 1633

Houtz and Sedlak method (2012) : 60 mM $K_2S_2O_8$ + 150 mM NaOH[1]

$$S_2O_8^{2-} + heat \rightarrow 2SO_4^{-\cdot} \quad (Reaction\ 1)$$

$$SO_4^{-\cdot} + OH^- \rightarrow SO_4^{2-} + \cdot OH^- \quad (Reaction\ 2)$$



In the USEPA 3rd Draft Method 1633, extracts are not concentrated after elution[2]

[1]Houtz&Sedlak (2012) https://doi.org/10.1021/es302274g

[2]https://www.epa.gov/system/files/documents/2021-09/method_1633_draft_aug-2021.pdf

Sample description and handling

The following samples were examined for the presence of PFASs and/or PFAA precursors using the optimized methods:

a) Three firefighting foam samples:

- Aqueous film forming foam (AFFF)
- Protein foam (PF)
- Synthetic surfactant foam (SSF)

b) Two Durable Water Repellent (DWR) samples

- DWR-2011-2
- DWR-2011-5

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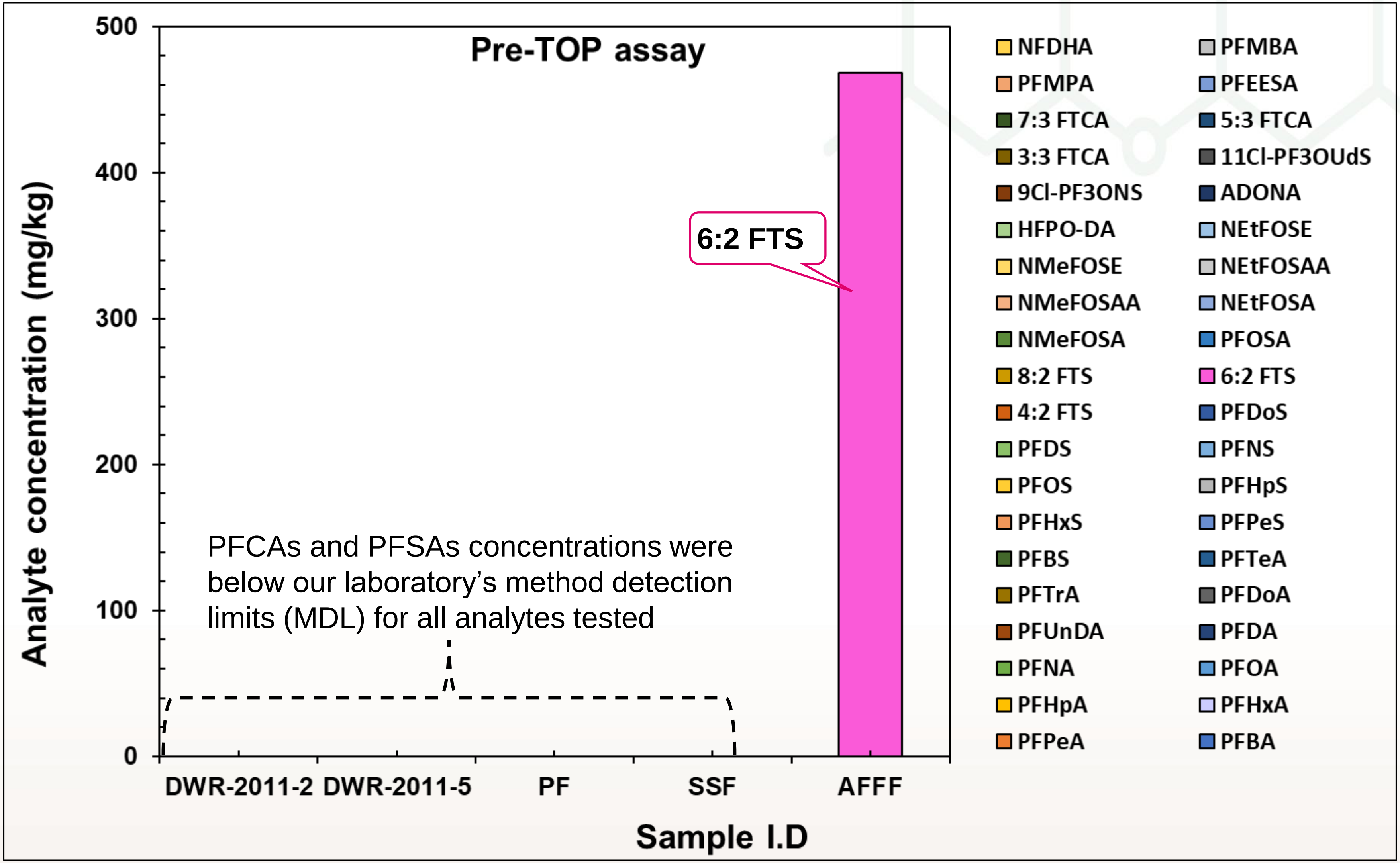
Optimized USEPA 3rd Draft Method 1633: Analyte and EIS recoveries

Analyte	Analyte recovery (%)	EIS recovery (%)	Analyte	Analyte recovery (%)	EIS recovery (%)
PFBA	96	79	6:2 FTS	116	98
PFPeA	108	86	8:2 FTS	121	131
PFHxA	95	83	PFOSA	112	108
PFHpA	126	82	NMeFOSA	106	46
PFOA	96	82	NEtFOSA	101	37
PFNA	132	80	NMeFOSAA	103	94
PFDA	112	85	NEtFOSAA	112	107
PFUnDA	113	84	NMeFOSE	115	61
PFDoA	106	80	NEtFOSE	109	63
PFTrA	91	89	HFPO-DA	96	79
PFTeDA	99	99	ADONA	113	79
PFBS	129	80	9Cl-PF3ONS	110	79
PFPeS	126	80	11Cl-PF3OUdS	98	79
PFHxS	109	80	3:3 FTCA	91	82
PFHpS	97	88	5:3 FTCA	105	79
PFOS	92	88	7:3FTCA	105	79
PFNS	99	88	PFEESA	117	79
PFDS	106	88	PFMPA	110	82
PFDoS	101	88	PFMBA	107	82
4:2 FTS	120	95	NFDHA	112	79

PFASs and PFAA precursors in DWR, AFFF, PF and SSF samples (Pre-TOP assay results)

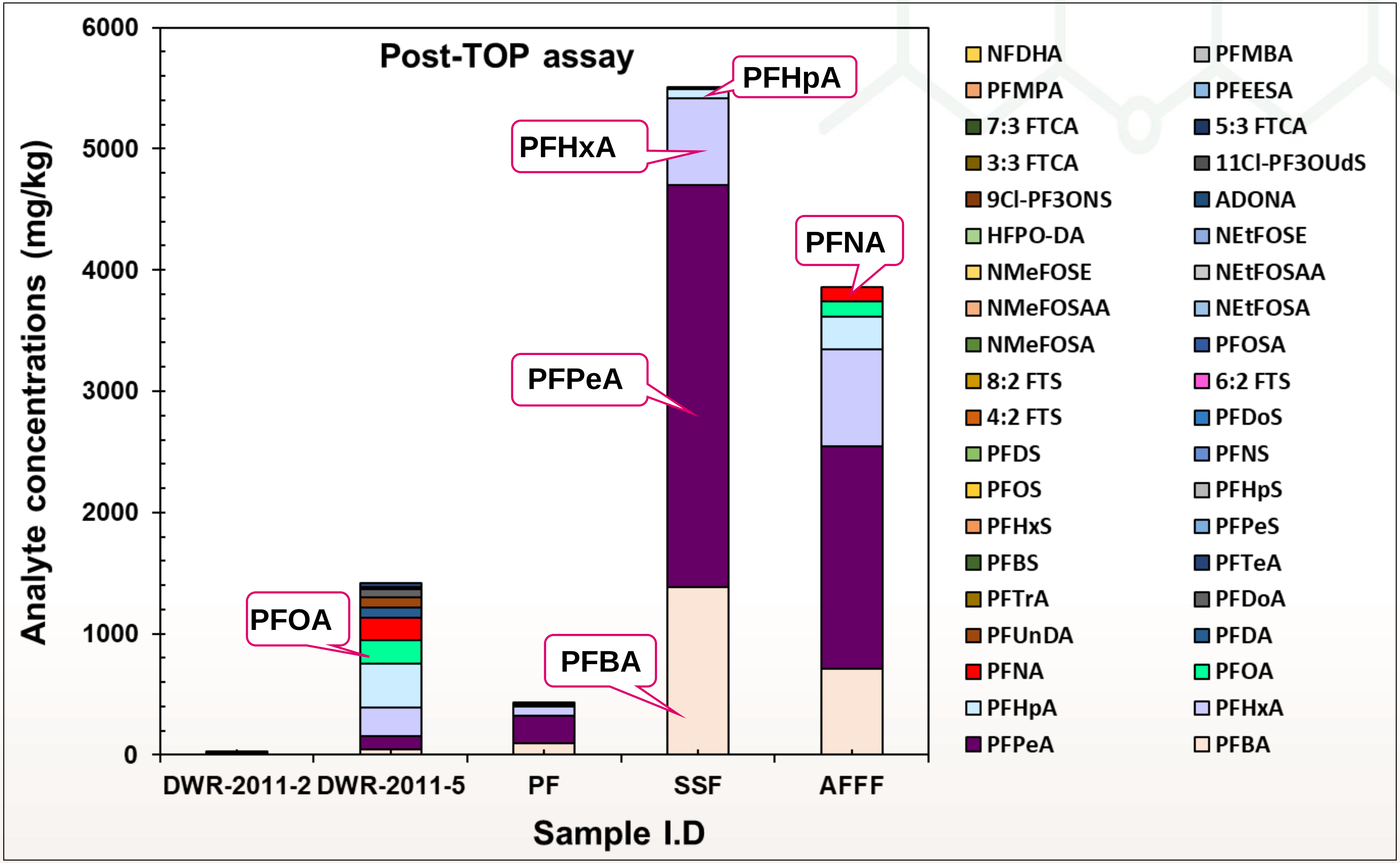


Perfluoroalkyl carboxylic acids (PFCAs)
Perfluoroalkane sulfonic acids (PFSAs)

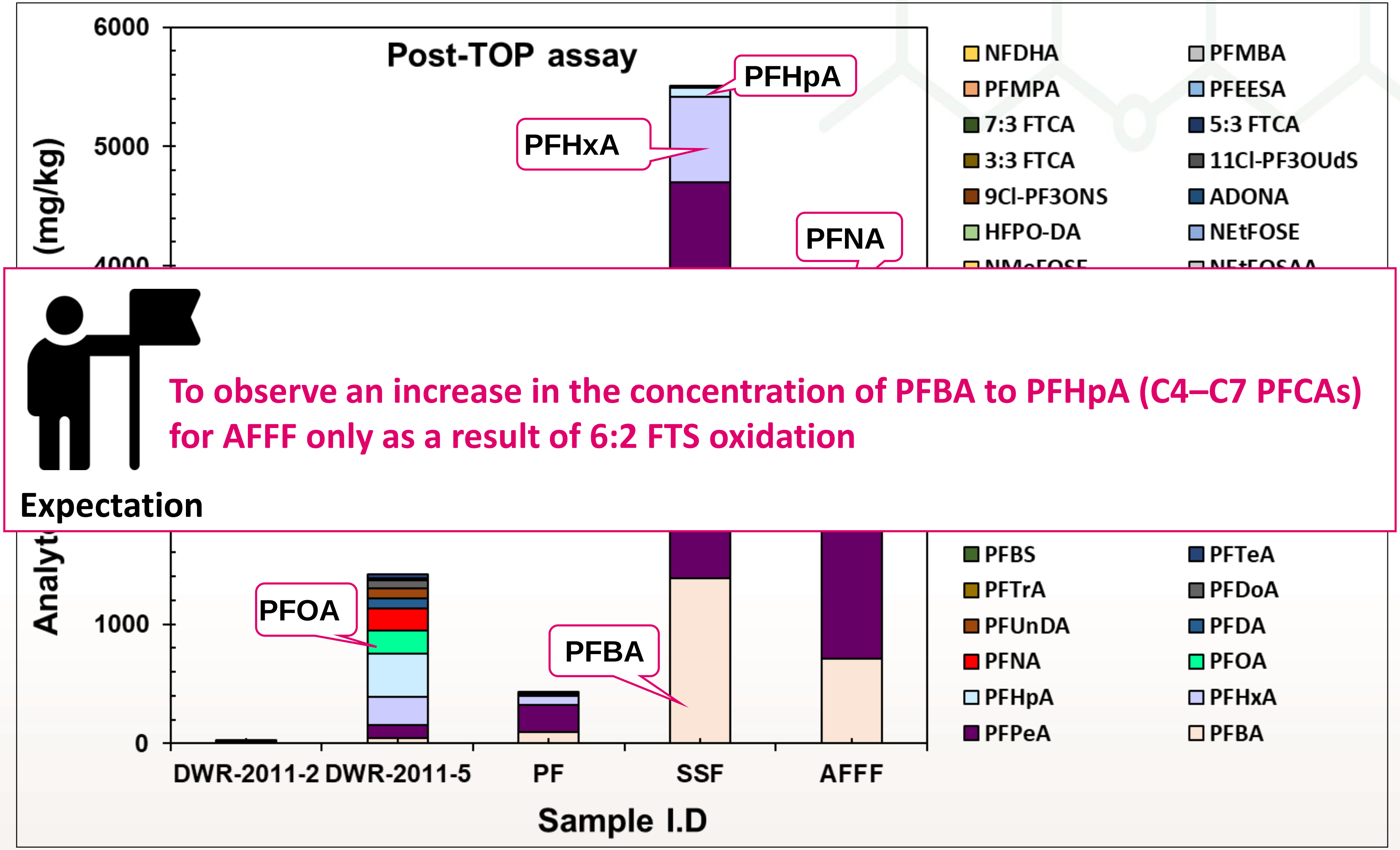
USEPA 3rd Draft Method 1633 Method Detection Limits (MDL)

Analyte	Method Detection Limit (MDL) (ng/mL)	Analyte	Method Detection Limit (MDL) (ng/mL)
PFBA	2.0	6:2 FTS	5.0
PFPeA	1.0	8:2 FTS	2.0
PFHxA	0.2	PFOSA	1.0
PFHpA	1.0	NMeFOSA	1.0
PFOA	1.0	NEtFOSA	1.0
PFNA	1.0	NMeFOSAA	2.0
PFDA	1.0	NEtFOSAA	2.0
PFUnA	1.0	NMeFOSE	5.0
PFDoA	1.0	NEtFOSE	10.0
PFTrA	1.0	HFPO-DA	2.0
PFTeA	0.2	ADONA	1.0
PFBS	0.5	9Cl-PF3ONS	2.0
PFPeS	1.0	11Cl-PF3OUdS	1.0
PFHxS	2.0	3:3 FTCA	5.0
PFHpS	1.0	5:3 FTCA	20.0
PFOS	2.0	7:3 FTCA	20.0
PFNS	1.0	PFEESA	1.0
PFDS	1.0	PFMPA	5.0
PFDoS	2.0	PFMBA	5.0
4:2 FTS	0.4	NFDHA	2.0

Post-TOP assay oxidation products in DWR, AFFF, PF and SSF samples



Post-TOP assay oxidation products in DWR, AFFF, PF and SSF samples



To observe an increase in the concentration of PFBA to PFHpA (C4–C7 PFCAs) for AFFF only as a result of 6:2 FTS oxidation

Expectation

Post-TOP assay oxidation products in DWR, AFFF, PF and SSF samples

Factors that could have contributed to the observed results

1. Limitations of currently available analytical methods

- Unidentified precursors resulted in the observed increase in the C4-C10 PFCAs concentrations post-TOP assay
- 8:2 fluorotelomer phosphate diester (8:2 diPAP) and 6:2 fluorotelomer phosphate diester (6:2 diPAP) are not included in the USEPA 3rd Draft Method 1633

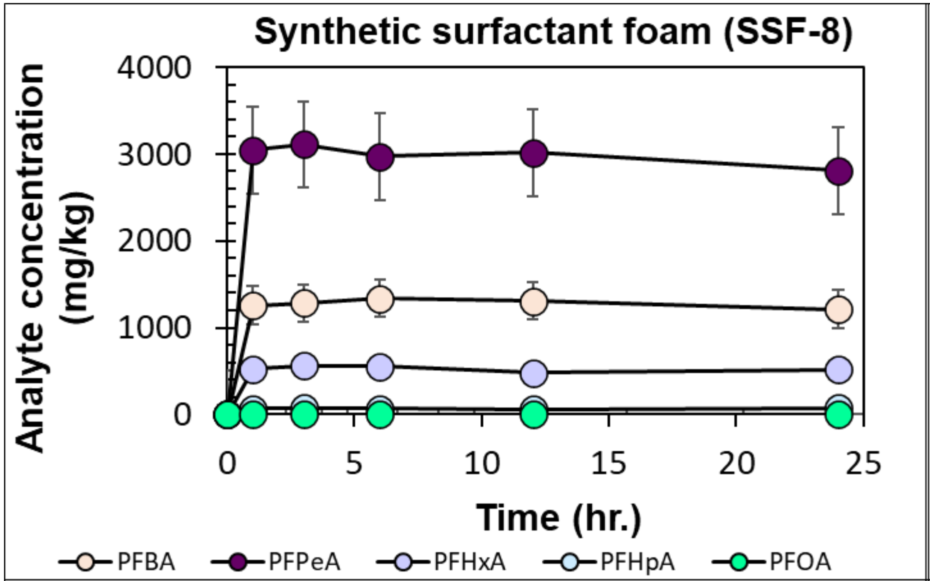
For example[1],

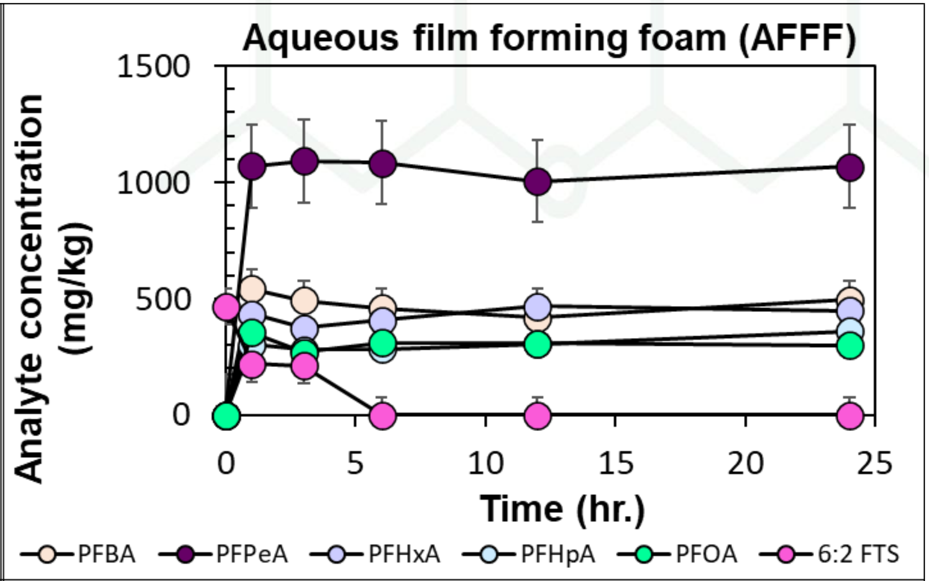
Table 1. Molar Yields of PFCAs from Precursors Thermolyzed in the Presence of Persulfate[a]

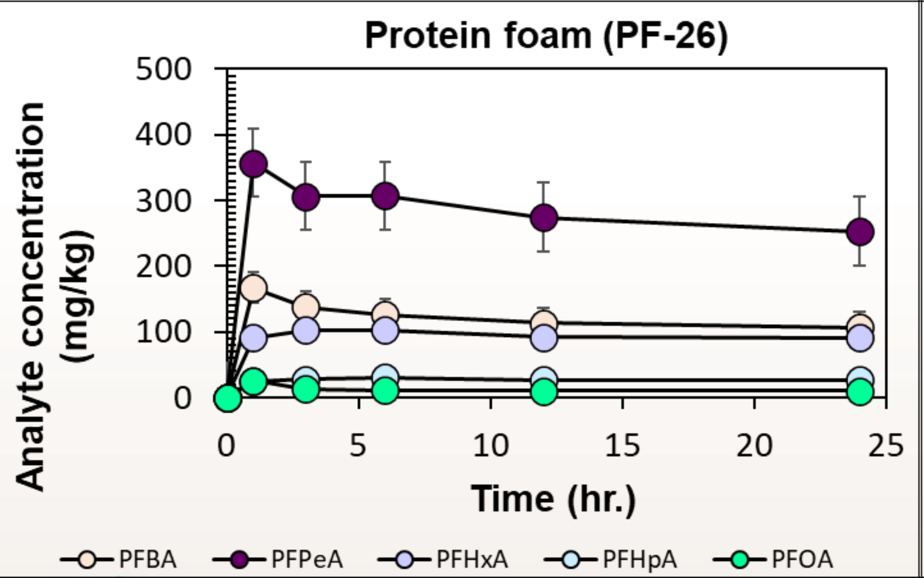
starting precursor compound	$[\text{persulfate}]_0$	$[\text{precursor}]_0$	$\Delta[\text{PFBA}]/[\text{precursor}]_0$	$\Delta[\text{PFPeA}]/[\text{precursor}]_0$	$\Delta[\text{PFHxA}]/[\text{precursor}]_0$	$\Delta[\text{PFHpA}]/[\text{precursor}]_0$	$\Delta[\text{PFOA}]/[\text{precursor}]_0$	$\Delta[\text{PFNA}]/[\text{precursor}]_0$
6:2 diPAP[b] ($n = 6$)	20 to 60 mM	25 μg/L	27% ± 3%	47% ± 3%	33% ± 2%	15% ± 3%		
8:2 diPAP[b] ($n = 6$)	20 to 60 mM	25 μg/L	10% ± 2%	17% ± 1%	24% ± 1%	43% ± 2%	38% ± 2%	13% ± 1%

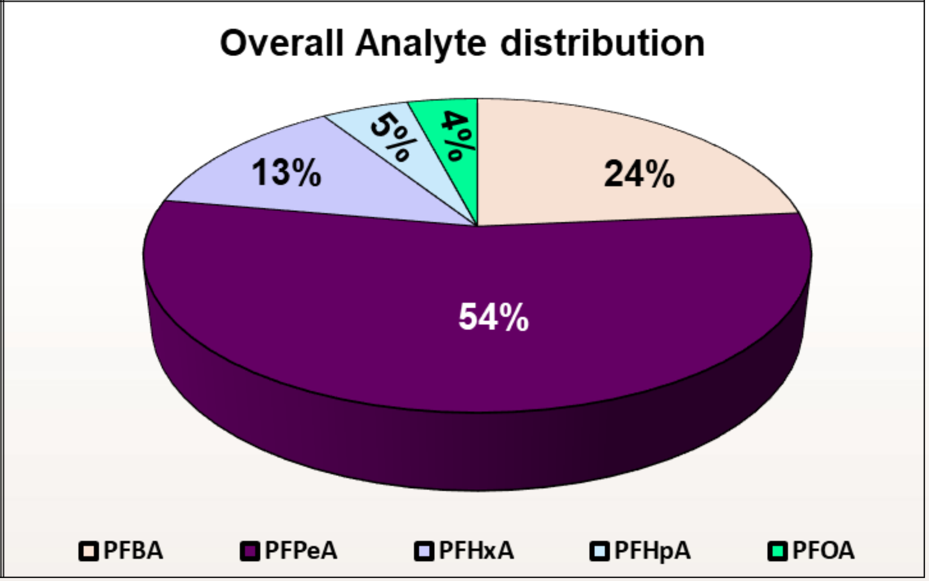
[1]Houtz&Sedlak (2012)
https://doi.org/10.1021/es302274g

Perfluoroalkyl acids (PFAAs) generation behavior during TOP assay









Perfluoroalkyl acids (PFAAs) generation behavior during TOP assay

Analyte	Time (hr.)	x̄ [PFBA] (mg/kg)	CV (%)	x̄ [PFPeA] (mg/kg)	CV (%)	x̄ [PFHxA] (mg/kg)	CV (%)	x̄ [PFHpA] (mg/kg)	CV (%)	x̄ [PFOA] (mg/kg)	CV (%)
SSF-8	0	0	0	0	0	0	0	0	0	0	0
	1	1258	4	3047	4	528	4	67	3	5	0
	3	1287	4	3110	3	558	4	72	6	5	12
	6	1339	4	2970	4	556	6	69	2	4	8
	12	1306	2	3016	4	484	9	63	2	3	13
	24	1214	8	2809	6	518	4	74	5	3	7
PF-26	Time (hr.)	x̄ [PFBA] (mg/kg)	CV (%)	x̄ [PFPeA] (mg/kg)	CV (%)	x̄ [PFHxA] (mg/kg)	CV (%)	x̄ [PFHpA] (mg/kg)	CV (%)	x̄ [PFOA] (mg/kg)	CV (%)
	0	0	0	0	0	0	0	0	0	0	0
	1	167	15	357	13	91	21	25	10	23	17
	3	137	7	306	9	102	9	28	5	13	9
	6	126	2	307	2	102	1	31	3	11	9
	12	113	7	274	7	92	6	27	6	10	3
	24	107	7	253	3	91	5	27	12	10	4
AFFF	Time (hr.)	x̄ [PFBA] (mg/kg)	CV (%)	x̄ [PFPeA] (mg/kg)	CV (%)	x̄ [PFHxA] (mg/kg)	CV (%)	x̄ [PFHpA] (mg/kg)	CV (%)	x̄ [PFOA] (mg/kg)	CV (%)
	0	0	0	0	0	0	0	0	0	0	0
	1	543	18	1069	9	434	7	304	9	313	9
	3	493	15	1091	8	375	4	281	3	270	15
	6	459	6	1085	4	407	8	285	4	310	3
	12	418	1	1005	3	469	12	306	6	309	19
	24	495	8	1068	9	448	9	360	9	266	15

- The test results (n=3) were generally good, although a larger variability (CV>10%) was observed for low concentrations and at shorter assay times

QA/QC of EPA 3rd Draft Method 1633 and TOP assay

EIS Compound	Recovery Range (%)			EIS Compound	Recovery Range (%)		
	pre-TOP assay	post-TOP assay	USEPA M1633		pre-TOP assay	post-TOP assay	USEPA M1633[5)]
$^{13}C_4$-PFBA	101-111	15-78	10-130*	$^{13}C_8$-PFOS	82-115	76-95	45-140
$^{13}C_5$-PFPeA	102-115	66-94	35-150	$^{13}C_2$-4:2FTS	71-89	57-68	60-200*
$^{13}C_5$-PFHxA	98-111	80-88	55-150	$^{13}C_2$-6:2FTS	70-98	54-69	60-200*
$^{13}C_4$-PFHpA	101-110	79-92	55-150	$^{13}C_2$-8:2FTS	60-85	52-74	50-200*
$^{13}C_8$-PFOA	96-121	85-98	60-140	$^{13}C_8$-PFOSA	98-113	89-100	30-130
$^{13}C_9$-PFNA	89-120	78-101	55-140	D_3-NMeFOSA	70-111	47-90	15-130
$^{13}C_6$-PFDA	87-111	78-95	50-140	D_5-NEtFOSA	57-111	49-85	10-130
$^{13}C_7$-PFUnA	88-108	76-84	30-140	D_3-NMeFOSAA	70-91	70-81	45-200*
$^{13}C_2$-PFDoA	77-111	72-98	10-150	D_5-NEtFOSAA	83-89	69-81	10-200
$^{13}C_2$-PFTeDA	81-115	49-83	10-130*	D_7-NMeFOSE	93-165	91-119	10-150*
$^{13}C_3$-PFBS	95-110	80-89	55-150	D_9-NEtFOSE	86-165	93-118	10-150*
$^{13}C_3$-PFHxS	89-106	76-97	55-150	$^{13}C_3$-HFPO-DA	93-105	74-94	25-160

All the Extractable Internal Standard (EIS) recoveries were within the acceptable ranges.

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TOP assay and PFAAs generation during TOP assay

- Pre-TOP assay, only 6:2 FTS was detected in the AFFF sample using USEPA 3rd Draft Method 1633
- C4–C8 PFCAs were the most abundant compounds in the post-TOP assay results for AFFF, PF, SSF and DWR samples
- Post-TOP assay, 6:2 FTS concentration was below our laboratory's lower detection limit, thus, it was assumed that 100% oxidation was achieved
- C4–C8 PFCAs generation trend was observed during TOP assay
- C4-C6 PFCAs generation: SSF-8 > AFFF > PF-26
- AFFF generated the highest C7-C8 PFCAs concentrations
- > 50% of the PFCAs generated is PFPeA

TOP assay method

Our in-house TOP assay method might be useful:

- For the quantification of PFAA precursors though not highly accurate
- As a cost-effective method for screening product and environmental samples in order to identify samples containing PFAA precursors

For example;

Identifying PFAA precursors

Using HRMS to identify PFAA precursors

Using reference standards to quantify expected PFAA precursors

Proposed cost-effective approach for identifying actual PFAS contamination

Using **TOP assay as a screening tool** to identify samples rich in PFAA precursors

↓

Identify PFAS compounds to which special attention should be paid to using HRMS

↓

Target analysis using reference standards

END